



## Luminescent nanophotonics and advanced solid state lasers

T.T. Basiev<sup>a</sup>, I.T. Basieva<sup>a,b,\*</sup>, M.E. Doroshenko<sup>a</sup>

<sup>a</sup> Laser Materials and Technology Center, A. M. Prokhorov General Physics Institute of RAS, Vavilova str. 38D, 119991 Moscow, Russia

<sup>b</sup> Linnaeus University, SE-351 95 Växjö, Sweden

### ARTICLE INFO

Available online 31 December 2011

#### Keywords:

Luminescence quenching  
Cooperative energy transfer  
Mid-IR lasers  
Laser ceramics

### ABSTRACT

In this review, authors present their latest findings in luminescence quenching kinetics theory and advanced solid state laser experiments. Luminescence quenching kinetics is a popular and exceptionally useful tool to analyze the nanosized luminophores and laser material nanostructure. Quenching kinetics may be multistage, some stages having a complex, not exponential, form. It is often the case for modern laser materials, which are nanostructured, and for particular cases of energy transfer (such as cooperative down-conversion). We present compact and easy-to-use analytical expressions and computer simulation for various cases of nonexponential quenching kinetics: migration-accelerated quenching in bulk material; cooperative luminescence quenching in bulk material; and two extreme cases of energy transfer in nanoparticles – static and with superfast migration (both including cooperative case of luminescence quenching in ensembles of acceptors comprised of two-, three-, and more particles). We also review the most perspective laser experiments lately performed in our laboratory, including those on fluoride laser nanoceramics and materials for middle infra-red lasers.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Nowadays, confined and nanostructured materials are of particular importance in physics of luminophores and laser media. Nanodispersed materials, photonic crystals and nanopowders doped by fluorescent ions, are very prospective for use in medicine, biology and optics.

By luminescent nanophotonics we mean not only photonics of nano-sized luminophores but also photonics of nanosized and nanostructured ensembles of luminescent particles in bulk laser materials and luminophores. One of the most important characteristics of luminescent objects is a kinetics of luminescence decay and quenching after short laser excitation. It allows one to directly connect macroscopic characteristics of luminophore radiation (such as decay time, quantum yield, doping concentration) with microscopic characteristics of active ions and molecules: absorption and emission cross-section, spontaneous radiation lifetimes, type of ion–ion multipole interaction, microefficiency of migration and quenching energy transfer and character of nanoscale doping distribution.

Since 1940s it has been known that kinetics of resonant nonradiative luminescence quenching of donors in an ensemble

of one-particle acceptors has nonexponential form due to averaging over donors with different (random) acceptor surroundings. By Förster and Galanin [1,2], kinetics of dipole–dipole donor–acceptor energy transfer was discovered to have a square root of time law. It was later [3–5] generalized to higher multiplicities  $S$  ( $S=6, 8, 10$  for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions) and different space dimensions  $d$  ( $d=1, 2, 3$ ) as  $I = \exp[-(Wt)^{d/S}]$ .

General description for three-dimensional case of static luminescence quenching (when efficiency of donor–donor interaction  $C_{DD}=0$ ) has the form, see, e.g., [6–8]:

$$I(t) = \begin{cases} \exp[-W_{in}t], W_{in} = 7c_A C_{DA}/R_{min}^S, & t < t_b \\ \exp[-(W_F t)^{3/5}], W_F = k c_A^{5/3} C_{DA}, & t > t_b, \end{cases} \quad (1a, b)$$

where  $W_{in}$  is the initial stage quenching rate,  $W_F$  is the quenching rate at disordered stage, described by Förster law,  $t_b$  is the boundary time between the stages,  $R_{min}$  is the minimal distance between optically active particles allowed in the material,  $k$  is a constant,  $c_A$  – acceptor particles concentration (proportion of the lattice sites occupied by acceptor particles in the sites available).

This two-stage form of kinetics can be used to obtain microefficiency and multipolarity of dominant ion–ion interaction, concentration dependence, level of particle ordering and restricted geometry features. From the kinetics slope in double logarithmic scale vs. logarithm of time we can find the fraction power of time  $d/S$  [6–8], and obtain multipolarity of interaction  $S$  or space dimension  $d$ . From the further analysis of Förster stage quenching rate, boundary time,

\* Corresponding author at: Laser Materials and Technology Center, A. M. Prokhorov General Physics Institute of RAS, Vavilova str. 38D, 119991 Moscow, Russia.

Tel.: +7 499 125 55 86; fax: +7 499 135 02 67.

E-mail address: [irina\\_basieva@lst.gpi.ru](mailto:irina_basieva@lst.gpi.ru) (I.T. Basieva).

initial stage quenching rate we can obtain microefficiency of donor–acceptor interaction  $C_{DA}$ , and minimum distance  $R_{\min}$ .

Generally speaking, as soon as we have a complex, not monoexponential, luminescence quenching kinetics, and we know its law, we have enough equations to find all the micro-parameters of the laser and fluorescent materials.

We have studied a number of cases where luminescence quenching kinetics has Förster-like stage. We always considered the situation of instant excitation of the material in which donor and acceptor ions are randomly distributed with small concentrations  $c_A$  and  $c_D$ . Donor excitation density is considered being small. Continuum approximation was used when deriving the analytical expressions, while computer simulation was performed using simple cubic lattice model.

## 2. Migration-accelerated quenching in bulk material

We would like to start with analyzing and testing the analytical solution for migration-accelerated quenching kinetics obtained more than 30 years ago by Russian scientist V.P. Sakun [9].

V.P. Sakun found corrections to the kinetics of luminescence quenching for the case of three-dimensional random walk of excitation. The expression for long time stage kinetics has the form similar to Eq. (1)(b) for static quenching:

$$I(t) \sim \exp\left[-(\gamma_D + \gamma_A)\sqrt{t}\right] \quad (2)$$

where  $\gamma_A = W_F^2 = (4\pi\sqrt{\pi}/3)c_A\sqrt{C_{DA}}$  is the macroparameter responsible for Förster static quenching, and the analogous parameter  $\gamma_D = (4\pi\sqrt{\pi}/3)c_D\sqrt{C_{DD}}$  depends on donor concentration  $c_D$  and microparameter of donor–donor interaction  $C_{DD}$ .

We have simulated the migration-accelerated kinetics for the pervasive set of parameters (donor and acceptor concentrations  $c_A$  and  $c_D$ , microefficiencies  $C_{DA}$  and  $C_{DD}$ ) in a simple cubic crystal lattice. We discovered that at least for a number of cases, the quenching kinetics does demonstrate a non-exponential long-time stage, which can be described by Eq. (2).

Let us note that the accurate simulation of the migration-accelerated quenching in bulk material demands large computational

resources, e.g., the results presented in Fig. 1 imply solving the differential equation systems of  $10^4 \times 10^4$  size.

In Fig. 1 we present the simulated kinetics (circles) for the case of  $\gamma_A/\gamma_D = 1.6$ , ( $c_A = 0.5\%$ ,  $c_D = 0.1\%$ ,  $C_{DD} = 0.1C_{DA}$ ) together with analytical expressions (1b) and (2), shown by dash lines. We can see that in the scale used  $-\ln(I)$  versus  $(t/t_0)^{1/2}$  where  $t_0$  is proportional to  $C_{DD}$ , kinetics are closely described by two linear stages – at first by Förster law (1b), and then by Eq. (2).

We would like to stress that Eq. (2) derived in [9] can be very useful for experimentalists when calculating the unknown micro and macro parameters of the quenching process and of the material they work with.

## 3. Cooperative luminescence quenching in bulk material

At first, let us consider kinetics of down conversion, or cooperative energy transfer from one donor simultaneously to two (or three, or  $n$ ) particle acceptors. By itself cooperative process of energy transfer has low probability, which made it hard to discover in the first up-conversion experiments [10,11]. However, in case of down-conversion [12–16], the probability is enhanced by a large factor – the number of final states or the number of combinations by  $n$  particles out of all lattice sites available for acceptors. Resulting cooperative quenching rate can be of the same order of magnitude or even an order higher than radiative decay [14]. Cooperative down-conversion is a way to transform radiation from UV and visible to infrared region, besides, it promises high efficiency, because for one pump photon we can expect to get two, or three lower frequency photons, that is 200% or 300% quantum efficiency.

We have studied this problem analytically, and have obtained a compact and clear analytical expression [17–19]:

$$I_n(t) = \exp[-(W_{\text{Fcoop}}t)^{d/q}], \quad q = nS - (n-1)d \quad (3)$$

where  $W_{\text{Fcoop}}$  is the average rate of cooperative quenching at Förster-like stage:

$$W_{\text{Fcoop}} = \left[ \Gamma\left(1 - \frac{d}{q}\right) \right]^{q/d} \left( \frac{d}{(S-d)} \right)^{(n-1)} \frac{c_A^{nS/d}}{(n-1)!} \frac{1}{t_0} \quad (4)$$

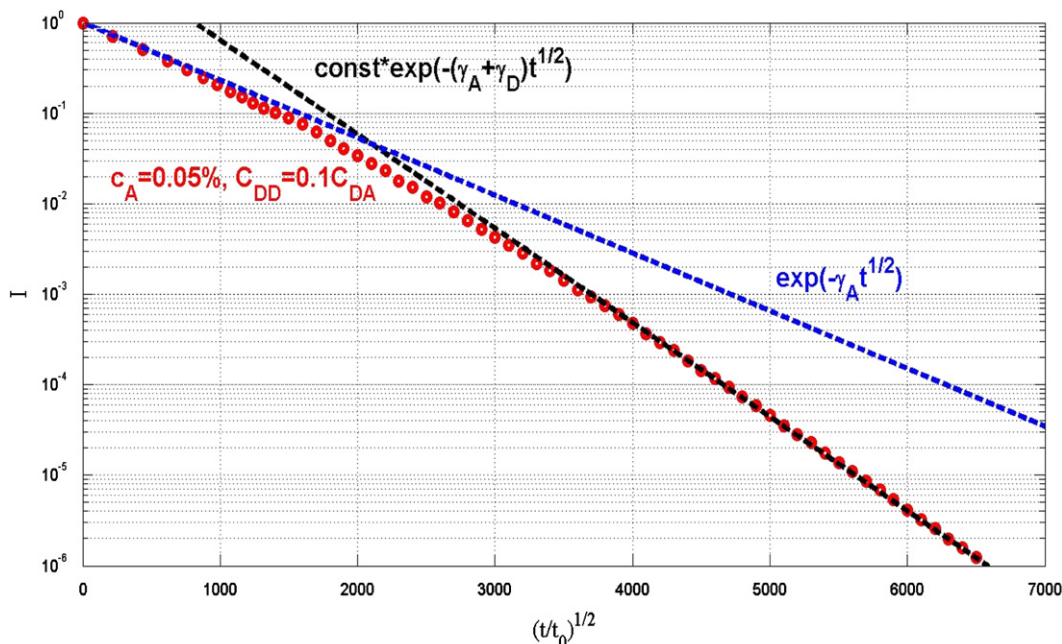


Fig. 1. Simulation of migration-accelerated hopping quenching in a bulk crystal having simple cubic lattice with interstitial distance of  $R_{\min} = 0.5$  nm. Parameters are:  $c_A = 0.05\%$ ,  $c_D = 0.1\%$ ,  $C_{DD} = 0.1C_{DA}$ ,  $C_{DA} = 1$  nm<sup>6</sup>/ms,  $t_0 = R_{\min}^6/C_{DD}$ .

Download English Version:

<https://daneshyari.com/en/article/5401427>

Download Persian Version:

<https://daneshyari.com/article/5401427>

[Daneshyari.com](https://daneshyari.com)