LASER APPLICATIONS AND OTHER TOPICS IN QUANTUM ELECTRONICS

Kinetics and quantum yield of photoluminescence of EuFOD$_3$ doped into a nanoporous glass with the help of supercritical CO$_2$

V.N. Bagratashvili, V.I. Gerasimova, V.M. Gordienko, S.I. Tsypina, E.A. Chutko

***Abstract*. The kinetics of photoluminescence of a EuFOD$_3$ metalloorganic compound doped into a nanoporous Vycor glass by the method of supercritical fluid impregnation is studied. The lifetime of luminescence of EuFOD$_3$ molecules in pores excited by an excimer XeCl laser was 40 µs, which is considerably smaller than this lifetime (150 – 890 µs) in solutions. The quantum yield of luminescence of EuFOD$_3$ was estimate as $\sim 4 \times 10^{-4}$.**

1. Introduction

Due to intense and long-lifetime luminescence and good solubility, europium beta-diketonates are widely used in scientific studies as luminescence marks in biology and medicine and in applied problems for manufacturing light diodes, UV radiation dosimeters, and AR coatings [1, 2]. One of these compounds is EuFOD$_3$ (FOD: 6,6,7,7,8,8,8-heptofluorine-2,2-dimethyl-3,5-octanedionate). This compound can be doped into nanoporous glasses and polymers by the method of supercritical fluid impregnation [3]. Optically transparent materials impregnated with rare-earth metals are promising for the development of integrated optical elements and three-dimensional memory [4, 5]. The use of such materials in applied problems depends on their absorption and luminescence spectra, radiation resistance, kinetics and quantum yield of luminescence.

The luminescence of solutions of europium beta-diketonates has been studied in many papers. In particular, the kinetics of EuFOD$_3$ luminescence in various solvents was investigated in paper [6]. However, the luminescent properties of molecules doped into porous transparent materials are changed due to the interaction of molecules with the surface of pores [7, 8]. Thus, variations in the spectral band intensities in the luminescence spectra of some europium beta-diketonates in silica gel were observed and the luminescence decay became two-exponential [7].

In this paper, we consider the luminescence kinetics of EuFOD$_3$ molecules doped into porous glass by means of supercritical CO$_2$. Supercritical CO$_2$ is carbon dioxide at the temperature and pressure exceeding critical values $T_{cr} = 31\,°C$ and $p_{cr} = 73.8$ atm. In this aggregate state, CO$_2$ represents something between liquid and gas: it can be compressed as gases and at the same time can dissolve solids. By saturating porous glass by EuFOD$_3$ molecules with the help of supercritical CO$_2$, we obtain a sample free of impurities (solvent residues). Therefore, the luminescence kinetics of the sample and its difference from this kinetics for molecules of the initial substance are determined only by the interaction of molecules with the walls of pores.

Figure 1 presents the energy level diagram of the EuFOD$_3$ molecule, which is typical for coordination europium compounds [1]. The position of the S$_1$ level was determined from the position of the absorption band maximum of EuFOD$_3$ in porous glass (Fig. 2) [3] and the T$_1$ level energy was estimated as $22000 - 23000$ cm^{-1} [9]. The EuFOD$_3$ molecule also has the level of charge transfer from the ligand to the metal. The absorption band corresponding to this level has a very low intensity and is not observed in the spectrum. This has led to uncertainties in the determination of the energy of this level, which varies according to data obtained by different researchers from 21300 cm^{-1} [9] to 27778 cm^{-1} [10]. The ligand absorbs UV radiation and undergoes the S$_0 \rightarrow$ S$_1$ transition to the first excited singlet state, from which the S$_1 \rightarrow$ T$_1$ intersystem crossing occurs to the triplet state. Then, energy transfer to the excited ^{5}D$_1$ level of the europium ion takes place, which is followed by vibrational relaxation from this level to the ^{5}D$_0$ level and red luminescence at the ^{5}D$_0 \rightarrow ^7$F$_j$ transitions, where $j = 0 - 6$. Along with luminescence transitions in Eu^{3+}, nonradiative relaxation occurs from the T$_1$ and ^{5}D$_0$ levels of Eu^{3+} and backward energy transfer from Eu^{3+} to the ligand [1]. Figure 2 also presents the luminescence spectrum of EuFOD$_3$ in a Vycor porous glass at the ^{5}D$_0 \rightarrow ^7$F$_2$ transition of Eu^{3+} ions excited by a XeCl laser.

V. N. Bagratashvili, S.I. Tsypina, E.A. Chutko Department of Perspective Laser Technologies, Institute of Laser and Information Technologies, Russian Academy of Sciences, ul. Pionerskaya 2, 142190 Troitsk, Moscow region; e-mail: chutko@mail.ru;
V.I. Gerasimova D.V. Skobel'tsyn Institute of Nuclear Physics, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia;
V.M. Gordienko Department of Physics, International Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia

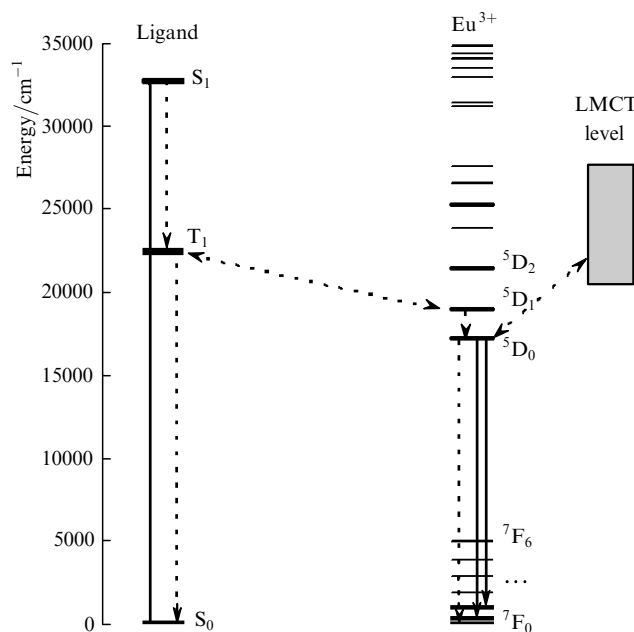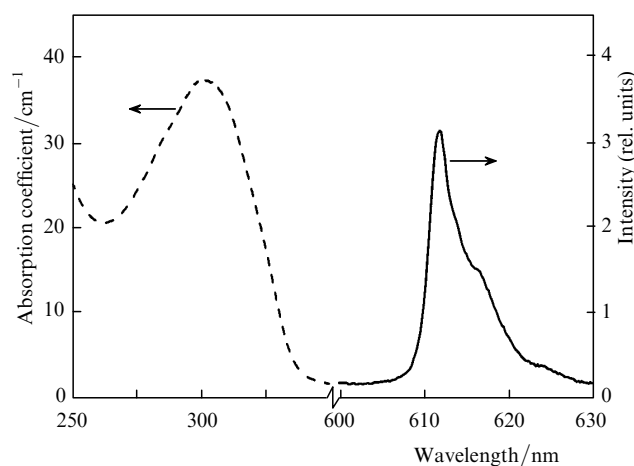**Figure 1.** Energy level diagram of the EuFOD$_3$ molecule. LMCT: ligand–metal charge transfer.

Figure 2. Absorption and luminescence spectra of nanoporous Vycor glass doped with EuFOD$_3$ at a concentration of 2.3×10^{17} cm^{-3} with the help of supercritical CO$_2$. Luminescence was excited by an LD(D)-400 deuterium lamp at 300 nm.

2. Experimental setup

The kinetics and quantum yield of luminescence of EuFOD$_3$ doped into porous glass were measured by using the experimental setup shown schematically in Fig. 3a. Radiation from an excimer XeCl laser emitting 308-nm (32468 cm^{-1}), 50-ns, 1-mJ pulses was focused by a lens L with a focal distance of 6 cm into a spot of area 0.03 cm^2 on a porous glass target T, which corresponded to the laser radiation energy density 3×10^{-5} J cm^2. Luminescence was detected perpendicular to the laser beam with a PD-24K photodiode. A 5-mm-thick KS11 optical filter F mounted between the side surface of the target and photodiode suppressed UV radiation scattered by the target. The output signal of the photodiode was fed to a Tektronix TDS-1012 oscilloscope.
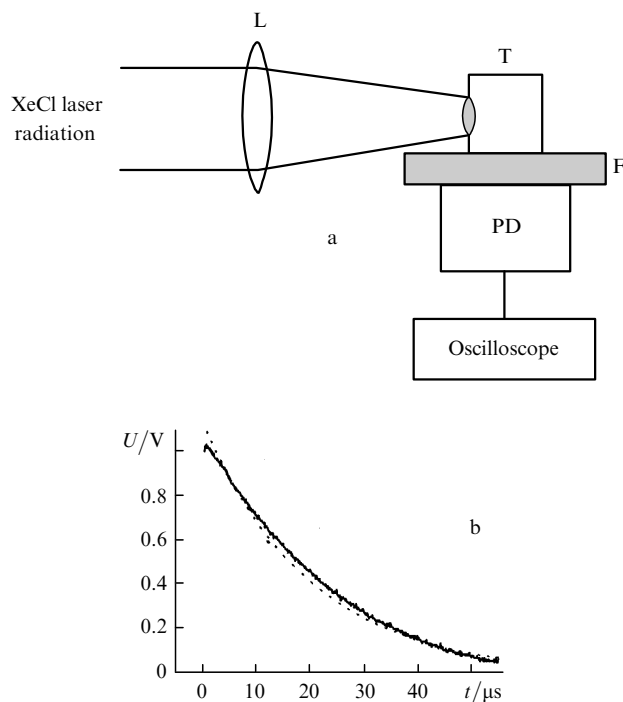

Figure 3. Scheme of the experimental setup for measuring the luminescence kinetics of EuFOD$_3$ doped into porous Vycor glass (a), and the output signal of the photodiode detecting UV radiation in a pure porous glass (solid curve) approximated by the function $y = y_0 \exp(-t/20 \text{ μs})$ (dashed curve) (b): (L) lens; (T) target; (F) filter; (PD) photodiode.

We determined preliminarily the instrumental function of the photodiode by measuring the intensity of laser radiation scattered in a pure porous glass. The output signal of the photodiode is approximated by the exponential $y = y_0 \exp(-t/\tau)$ with the characteristic time $\tau = 20$ μs (Fig. 3b). Because the laser pulse duration is 50 ns, this signal represents the instrumental function of the photodiode.

We studied 1.5-mm-thick Porous Vycor glass plates (Bioanalytical Systems Inc., USA) with pores of average size 4 nm. The EuFOD$_3$ polycrystalline powder (Aldrich Chemical Comp., USA) was doped into nanoporous Vycor glass at a temperature of 60 °C and a pressure of 140 atm. The impregnation procedure is described in detail in paper [11]. The concentration of EuFOD$_3$ in supercritical CO$_2$ was 3×10^{18} cm^{-3}, doping was performed for an hour. As shown in [3], this concentration of EuFOD$_3$ in supercritical CO$_2$ corresponds to the concentration of these molecules in porous glass equal to 2.4×10^{18} cm^{-3}. The absorption coefficient at 308 nm for this concentration is ~ 300 cm^{-1}. Thus, laser radiation penetrates only into the ~ 30-μm-thick surface layer of the impregnated sample. In this case, we observed visually the red luminescence of europium ions in the surface layer of the target.

The experimental setup for recording absorption and luminescence spectra is described in detail in [3].

3. Experimental results

3.1 Photoluminescence kinetics

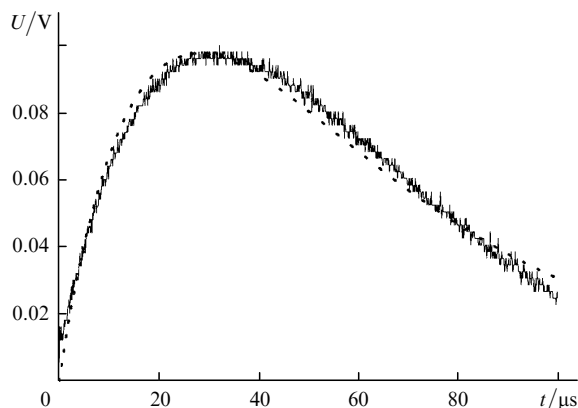The luminescence signal of EuFOD$_3$ in porous glass is presented in Fig. 4. One can see that the signal achieves a

Figure 4. Output signal of the PD-24K photodiode detecting the luminescence of EuFOD$_3$ doped into porous glass excited by a UV laser (solid curve) and the approximation of this signal by the function $y = 0.4[\exp(-t/40\ \mu s) - \exp(-t/20\ \mu s)]$ (dashed curve).

maximum within $\sim 30\ \mu s$ after the laser pulse and then slowly decreases. The decay time of the signal is comparable with the characteristic time of the instrumental function of the photodiode, which considerably affects the experimental dependence of the signal intensity. Let us assume that the real luminescence kinetics of EuFOD$_3$ in porous glass is described by the exponential $x = x_0 \exp(-t/t_{lum})$ with the luminescence lifetime t_{lum}. Then, the observed output signal of the photodiode can be described by the expression

$$y(t) = \int_0^t x_0 \exp(-t'/t_{lum}) y_0 \exp[-(t-t')/\tau] \mathrm{d}t'$$

$$= \mathrm{const} \cdot [\exp(-t/t_{lum}) - \exp(-t/\tau)]. \quad (1)$$

By approximating the experimental dependence by expression (1), we obtain $t_{lum} = 40 \pm 0.3\ \mu s$. Figure 4 shows that expression (1) well describes the experimental dependence.

3.2 Quantum yield of photoluminescence

The quantum yield of luminescence was estimated from the luminescence signal and laser pulse energy. The PD-24K photodiode was calibrated by radiation from a dye laser at 616 nm by using an ILD 2M power meter. According to the photodiode calibration, taking into account its receiving solid angle, the luminescence energy detected with the photodiode was (in μJ)

$$E_{lum} = 0.5\ \mu J\ W^{-1}\ \frac{W}{20\ \mu s}, \quad (2)$$

where $W = \int_0^\infty y(t) \mathrm{d}t \approx 7\ V\ \mu s$ is the integral luminescence signal detected with the photodiode. Therefore, $E_{lum} = 0.2\ \mu J$, which corresponds to emission of $N_{lum} \approx 7 \times 10^{11}$ 2-eV luminescence photons of the EuFOD$_3$ molecule.

As mentioned above, the laser pulse energy in our experiments was 1 mJ, which corresponds to $N \approx 1.6 \times 10^{15}$ of laser photons of energy 4 eV. Therefore, the quantum yield of luminescence of EuFOD$_3$ molecules is $k = N_{lum}/N \sim 4 \times 10^{-4}$.

4. Discussion of results

The exponential decay of the luminescence pulse of EuFOD$_3$ observed in porous glass is similar to the decay

of luminescence pulses of the EuFOD$_3$ powder and EuFOD$_3$ in various solvents. However, the luminescence lifetime $t_{lum} = 40\ \mu s$ of EuFOD$_3$ in porous glass proved to be considerably shorter than that in solvents and powder. The decay time of the luminescence signal corresponding to the 1/e level, obtained in different papers, varied from 0.15 to 0.89 ms depending on the solvent and was 0.62 ms for the EuFOD$_3$ powder excited at 337 nm (29674 cm^{-1}) [6].

Consider possible reasons for the rapid luminescence decay. The shortening of the luminescence lifetime of Er^{3+} ions is usually explained by the increase in the nonradiative relaxation of the $^5D_0$ level [1]. This level in EuFOD$_3$ has the following channels of nonradiative relaxation [6, 9]:

(i) Energy transfer to the vibrational levels of OH groups located near the Eu^{3+} ion;

(ii) nonradiative relaxation accompanied by the charge transfer from the ligand to metal;

(iii) backward energy transfer to the triplet level of the ligand.

We assume that the number of OH groups near europium ions in EuFOD$_3$ molecules doped into porous glass can be increased due to the interaction of these molecules with the walls of pores, which are 'covered' by the OH monolayer in the Vycor glass in the air atmosphere [12].

The rates on nonradiative relaxation with the chare transfer from the ligand to metal and of backward energy transfer to the triplet level of the ligand depend on temperature. Let us estimate the laser-induced increase in the temperature of porous glass from the expression

$$\Delta T = \frac{E}{cm} = \frac{10^{-3}\ J}{0.75\ J\ g^{-1}\ K^{-1}(1.35 \times 10^{-4}\ g)} \approx 10\ K, \quad (3)$$

where E is the absorbed laser pulse energy; $c = 0.18\ \mathrm{cal}\ g^{-1}\ K^{-1} = 0.75\ J\ g^{-1}\ K^{-1}$ is the heat capacity of porous glass [12]; $m = S\Delta l\rho$ is the mass of the porous glass absorbing laser radiation; $S = 0.03\ \mathrm{cm}^2$ is the laser spot area; $\Delta l = 3 \times 10^{-3}$ is the surface layer thickness in which the laser pulse is absorbed; and $\rho = 1.5\ \mathrm{g\ cm}^{-3}$ is the porous glass density [12]. According to [9], the increase in the glass temperature by 10 K reduces the luminescence lifetime by 20 μs, i.e. the 'temperature quenching' cannot explain such a rapid luminescence decay of EuFOD$_3$ in porous glass. However, it is not inconceivable that the charge-transfer level and the triplet level of the ligand of EuFOD$_3$ molecules in pores are shifted so that nonradiative relaxation becomes more efficient.

5. Conclusions

We have measured the luminescence kinetics and quantum yield for EuFOD$_3$ molecules doped into porous glass. The luminescence lifetime 40 μs proved to be considerably shorter than that for EuFOD$_3$ in solutions and powder. We assume that this is caused by the increase in the number of OH groups near europium ions in EuFOD$_3$ molecules interacting with the walls of pores.

References

1. De Sa G.F., Malta O.L., de Mello Donega C., Simas A.M., Longo R.L., Santa-Cruz P.A., da Silva E.F. Jr. *Coord. Chem. Rev.*, **196**, 165 (2000).
2. Ci Y.X., Yang X.D., Chang W.B. *J. Immunol. Methods*, **170**, 233 (1995).
3. Gerasimova V.I., Zavorotnyi Yu.S., Rybaltovskii A.O., Taraeva A.Yu., Tsypina S.I., Bagratashvili V.N. *Opt. Spektrosk.*, **98**, 616 (2005).
4. Miura K., Qiu J., Fujiwara S., Sakaguchi S., Hirao K. *Appl. Phys. Lett.*, **80**, 2263 (2002).
5. Chutko E.A., Tsypina S.I., Sviridova A.A., Bagratashvili V.N. *Proc. SPIE Int. Soc. Opt. Eng.*, **5399**, 115 (2004).
6. Villata L.S., Wolcan E., Feliz M.R., Capparelli A.L. *J. Photochem. Photobiol. A*, **115** 185 (1998).
7. Strek W., Sokolnicki J., Legendzievich J., Maruszewski K., Reisfeld R., Pavich T. *Opt. Mater.*, **13**, 41 (1999).
8. Meneses-Nava M.A., Barbosa-Garsia O., Diaz-Torres L.A., Chaves-Cerda S., King T.A. *Opt. Mater.*, **13**, 327 (1999).
9. Villata L.S., Wolcan E., Feliz M.R., Capparelli A.L. *J. Phys. Chem.*, **103**, 5661 (1999).
10. Gerasimova V.I., Zavorotnyi Yu.S., Rybaltovskii A.O., Lemenovskii D.A., Timofeeva V.A. *Kvantovaya Elektron.*, **36**, 791 (2006) [*Quantum Electron.*, **36**, 791 (2006)].
11. Bagratashvili V.N., Zavorotnyi Yu.S., Popov V.K., Rybaltovskii A.O., Tsypina S.I., Chernov P.V. *Perspekt. Mater.*, (1), 35 (2002).
12. Elmer T.H., in *Engineered Materials Handbook. Vol. 4. Ceramic and glasses* (Detroit: ASM Int., 1991) p. 427; http://www.corning.com/lightingmaterials/images/porous.pdf.